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RESEARCH REPORT

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HEATS OF FORMATION OF COMPOUNDS
CONTAINING B, Be, Al AND Li

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HEATS OF FORMATION OF COMPOUNDS
CONTAINING B, Be, Al and Li

1. SUMMARY OF THE WORK ACCOMPLISHED

A. Beryllium Fluoride

Final evaluation of the measurements on beryllium fluoride has been deferred. Experiments on the preparation of a completely crystalline beryllium fluoride by various methods have, so far, not succeeded.

B. Double Oxides

The working of the platinum calorimeter has been simplified and the precision increased by maintaining the samples at constant temperature in a small metal block thermostat before dropping them into the calorimeter.

Solution experiments on the compound $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$ and on mixtures of gibbsite and boron oxide (glass) in the corresponding ratio have been made. Eight experiments on the mixture gave $\Delta H'_{\text{sol}} = 799.3 \pm 1.0$ kcal for the molar heat of solution. Seven experiments on the compound gave $\Delta H'_{\text{sol}} = 900.0 \pm 1.4$ kcal for the molar heat of solution. From these measurements and Barany's [Koehler, Barany and Kelley, Bureau of Mines Report of Investigations 5711 (1961)] heat of formation of gibbsite from α -alumina and water ($\Delta H_{\text{hydr. 298}}^\circ = -7.36 \pm 0.62$ kcal), the preliminary value $\Delta H_{\text{f 298}}^\circ = +27.4 \pm 5.8$ kcal is derived for the heat of combination of the oxides in $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$. This value is subject to corrections for small errors in the calibration of the calorimeter, in the estimate of the heat of

dilution of the concentrated hydrofluoric acid solution by the water of the gibbsite and for a possible error in the heat of formation of gibbsite.

Several measurements on the heat of solution of the compound $\text{Al}_2\text{O}_3 \cdot \text{Li}_2\text{O}$ and corresponding mixtures of lithia and gibbsite have been made.

When, in experiments on the preparation of the compound $5\text{Al}_2\text{O}_3 \cdot \text{Li}_2\text{O}$ in a completely anhydrous and soluble form, the constituent oxides were heated to temperatures below 900°C , reaction was incomplete. At $1,000^\circ\text{C}$ or higher temperatures, the double compound became largely insoluble. Preparation of chrysoberyl, $\text{Al}_2\text{O}_3 \cdot \text{BeO}$ [according to the method briefly described by Lang, Fillmore and Maxwell, J. Res. N.B.S. 48, 298, (1952)] gave X-ray patterns which, in addition to lines due to chrysoberyl, showed further lines possibly due to $\text{Al}_2\text{O}_3 \cdot 3\text{BeO}$.

C. Mixed Fluorides

Li_3AlF_6

X-ray powder photographs of Li_3AlF_6 in a wide temperature range have been taken. The existence of various forms of the compound designated α , β , γ , δ and ϵ in order of stability at increasing temperature has become evident. An extremely slow conversion of α into β occurs when the α form is heated to 225°C ($\pm 50^\circ\text{C}$), but the direct reconversion of β into α has not been observed. The β form is transformed into γ at 475°C ($\pm 10^\circ\text{C}$). On slow cooling the γ form is converted into β which is retained on further cooling to room temperature. If the γ form is rapidly cooled, the product obtained after some time at room temperature is a mixture of α and β . The γ form is transformed into δ at

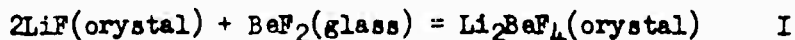
575°C ($\pm 10^\circ\text{C}$) and the δ form into the ϵ form at 705°C ($\pm 10^\circ\text{C}$). The conversions $\gamma - \delta$ and $\delta - \epsilon$ are readily reversible. The product in the calorimetric experiments is thus a mixture of α , β and supercooled γ which slowly changes into α .

The endothermic reaction (~ 0.9 kcal) obtained on reheating the product is therefore explained by both effects mentioned in Administrative Report No. 17, I.D., i.e. retention of γ and some evaporation of LiAlF_4 . The conversion $\alpha - \beta$ is probably thermochemically negligible and the most probable value for the heat of combination of the two single fluorides to form α - or β - Li_3AlF_6 is therefore $\Delta H_{f298}^\circ = -5.5 (\pm 0.5 \text{ kcal})$.

The various phase changes reported here are not likely to seriously invalidate the heat capacity measurement of Li_3AlF_6 [Douglas and Neuffer, N.B.S. Report 8186, Jan. 1964] so that the value for the entropy $S_{298}(\text{Li}_3\text{AlF}_6) = 45.04 \text{ e.u.}$ derived from them and the heat measurements reported here cannot be significantly in error.

Li_2BeF_4

The heat of the reaction



has been measured by heating the constituents within the small furnace in the calorimeter. Very thorough mixing of the single fluorides is necessary apparently because of the extremely high viscosity (low electrical conductivity) of molten BeF_2 . From five experiments in which this precaution was taken, a value $\Delta H_r^\circ = -5.3 \pm 0.5 \text{ kcal}$ has been derived for the heat of reaction I. The product has been identified by powder X-ray photography as the normal crystalline form [α in the designation of Novaslova, Simanov and Yarembash, Zhur. Fiz. Khim., 26, 1244, (1952)]. On

reheating the product after several hours at room temperature, a barely detectable endothermic heat effect is observed. This cannot be readily explained at present. This is taken care of if one assumes for the heat of formation of α - Li_2BeF_4 from the constituents $\Delta H_f^\circ = -5.5 \pm 0.7$ kcal.

2. WORK IN THE NEXT PERIOD

A. Beryllium Fluoride

Further attempts to prepare BeF_2 in a complete crystalline state will be made with a view to determining the heat of glass - crystal transition. Addition of lithium fluoride will be made to the mixture for the Be-PbF₂ reaction in order to form the crystalline compound Li_2BeF_4 .

B. Mixed Oxides

Measurements in the Al_2O_3 - B_2O_3 system will be completed. Measurements in the Al_2O_3 - Li_2O system will continue. If a completely anhydrous and soluble $5\text{Al}_2\text{O}_3 \cdot \text{Li}_2\text{O}$ cannot be made, the previous preparation which contains about 2 weight per cent water will be used. Measurements on either the heat of formation of gibbsite or of compounds in the Al_2O_3 - BeO system, if available, will be made.

One further attempt to prepare $5\text{Al}_2\text{O}_3 \cdot \text{Li}_2\text{O}$ in a completely anhydrous and soluble form will be made. Investigations on the preparation of the compounds in the Al_2O_3 - BeO system in a well defined and hydrofluoric acid soluble state will continue.

C. Mixed Fluorides

Investigations in the BeF_2 - LiF system will continue. Of the various double compounds suggested, the existence of LiBeF_3 seems undisputed, but careful thermochemical study will be necessary to ascertain whether it is stable or metastable with respect to disproportionation into BeF_2 and Li_2BeF_4 .

3. No inventions were conceived or made during the period.
4. No personnel changes or other significant administrative actions occurred during the period.

Dr. Gross visited the United States from the 13th - 30th October 1964. He discussed progress of the work with Dr. Joseph F. Masi and Major C. J. Donovan of the Office of Scientific Research, United States Air Force; he visited several laboratories and had scientific discussions with various United States thermochemists. He attended the 19th Calorimetry Conference in Washington, D.C., and Bethesda, Md., and reported on "Heats of Formation of α' -Beryllium Chloride and α - and β -Beryllium Nitride", an investigation which had been entirely sponsored by the Air Force Office of Scientific Research.

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